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Final Technical Report

AFOSR 91-0189

For the Period: May 1, 1991 - April 30, 1994

Date: June 29, 1994

Research on Organofluorine Chemistry for  
700 Degrees F Thermooxidative Stability

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Jean'ne M. Shreeve  
Robert L. Kirchmeier  
Department of Chemistry  
University of Idaho  
Moscow, ID 83843

### Abstract

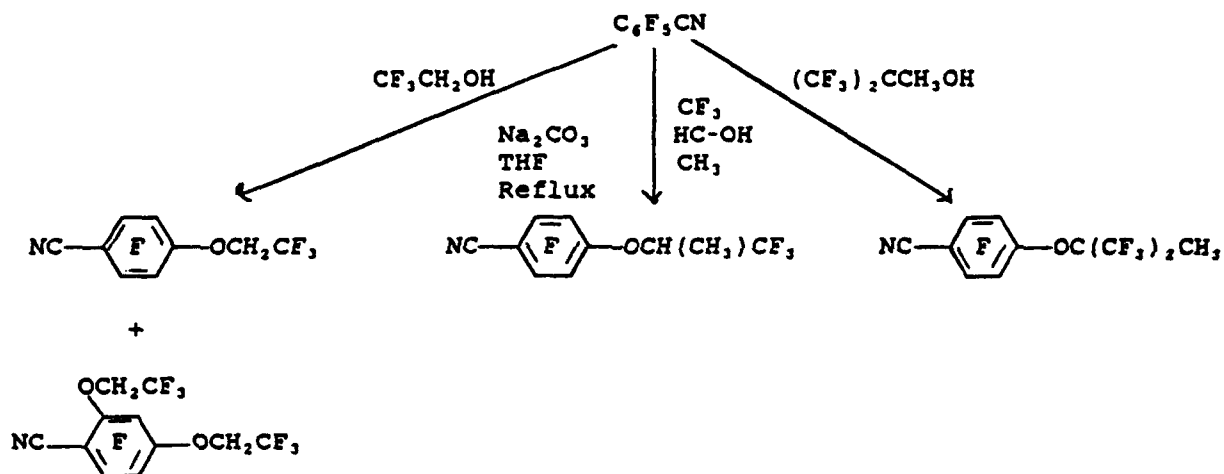
Much exciting chemistry has been completed over the three year course of this grant. The 32-membered fluorinated multifunctional heterocycle  $(C(O)N(CH_3)SO_2(CF_2)_2O(CF_2)_2O(CF_2)_2SO_2(CH_3)NC(O))_2$  was prepared and a crystal structure was obtained. New, efficient routes for the preparation of fluorinated amines and azaalkenes have been developed, and several members of a nearly unknown class of compounds, i.e., fluoroalkyl(aryl)tetraazanes were prepared and characterized. Methods were also developed for the synthesis of perfluoropropylidene containing aromatic and alkyl ethers.  $R_f$  transfer reagents, e.g.,  $CF_3Si(CH_3)_3$  and  $C_6F_5Si(CH_3)_3$ , as well as  $R_fOSi(CH_3)_3$ , were prepared and applied to the preparation of novel ethers, and substituted aromatic compounds. Several fluorinated macroheterocycles were synthesized using multifunctional silanes and siloxanes. The chemistry of perfluorovinylamines has been explored in some detail.

Highlights

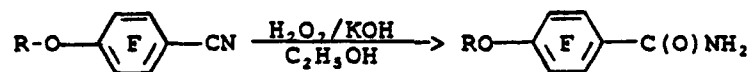
1. Developed useful, high yield synthetic routes to polyfluorinated amines and azaalkenes.
2. Synthesized poly and perfluoroalkyl(aryl)tetrazanes, and studied characteristics as a function of structure. Previously this class of compounds consisted of only a single example.
3. Development of  $R_f$  transfer reagents using silanes and siloxanes.
4. Synthesis of large, polyfluorinated heterocycles, and crystal structure of a 32-membered polyfluorinated heterocycle.
5. Development of methods for incorporating perfluoropropylidene groups into aromatic and other ethers.

I. Year 1: May 1, 1991 to April 30, 1992

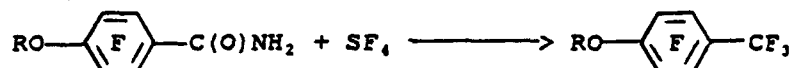
Polyfluorinated alcohols have been reacted under reflux with pentafluorobenzonitrile to give mono- and disubstituted polyfluorinated aryl ethers in moderate to good yield.



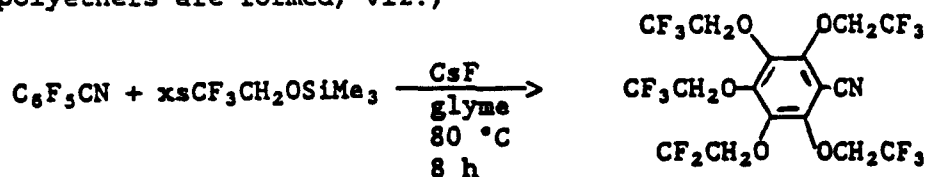
The products can be readily converted to amides, i.e.,



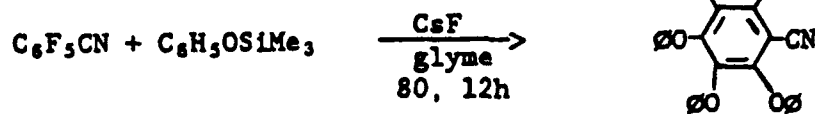
Conversion of these amides to the trifluoromethyl functionality via reaction with  $\text{SF}_6$  is easily done.



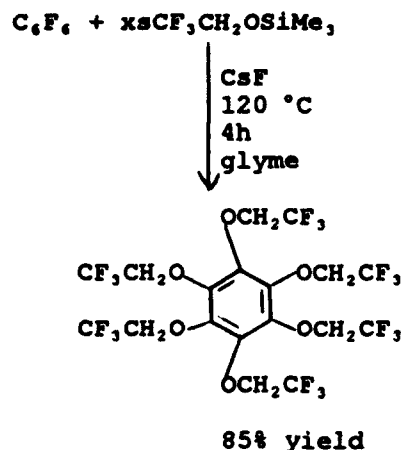
Polyfluorinated siloxanes provide a much better route to these polyethers when reacted with pentafluorocyanobenzene in the presence of catalytic amounts of fluoride ion. The yields obtained are generally much higher. Furthermore, when excess siloxane is used, highly interesting and unusual polyethers are formed, viz.,



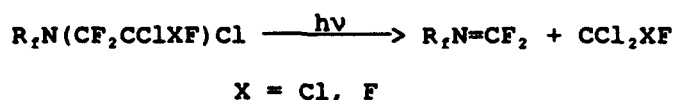
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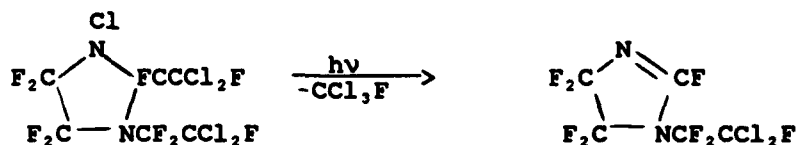
With hexafluorobenzene, similar derivatization is easily achieved, although at slightly higher temperature.



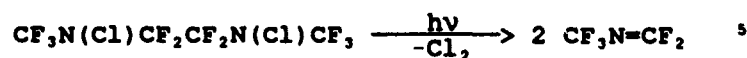
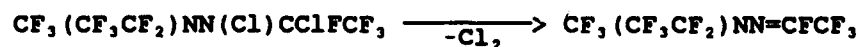
Previously published routes to per- or polyfluoroazaalkenes often require high temperature and/or subsequent fluorination or the yields may be low. We reported and continue to utilize a convenient, facile route for the high yield preparation of azaalkenes by photolysis of selected chloro(perfluoroalkyl) (chlorofluoro- alkyl)amines,  $\text{R}_2\text{N}(\text{R}_1')\text{Cl}$ , with concomitant loss of C-1 chlorofluorocarbons, or chlorine. For example, photolysis of monochloroamines



as well as heterocyclic chloroamines



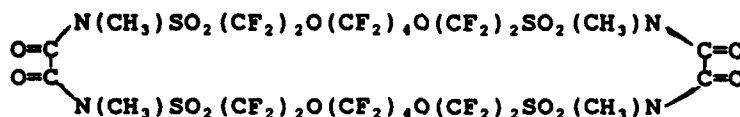
gives high yields of azaalkenes, via the loss of  $\text{CF}_2\text{Cl}_2$  or  $\text{CCl}_2\text{F}$ . In some instances when the terminal carbon-containing substituent  $\beta$  to the N-Cl moiety is highly fluorinated, azaalkene formation is accompanied by loss of chlorine, e.g.,



We also reported the syntheses of some new azaalkenes and some reactions

of azaalkenes which take advantage of the reactivity of the carbon-nitrogen double bond or the carbon-fluorine bonds at the azene carbon. Additionally, it now is possible to synthesize a stable tetraazane that contains eight nitrogen atoms, i.e., the stable, involatile tetraazane  $(\text{NF}_2\text{CF}_2\text{CF}_2\text{N}(\text{CF}_3)\text{N}(\text{CF}_2\text{CF}_2\text{NF}_2)\text{N}(\text{CF}_2\text{CF}_2\text{NF}_2))_2$ . The existence of this and other high nitrogen compounds is supported by spectral data and elemental analysis.

We reported the synthesis and structure of a unique, polyfluorinated thirty-two-membered multifunctional heterocyclic ring. As shown below, the ring contains four N-methyl sulfonamide, two  $\alpha$ ,  $\beta$ -diketone, and four ether functional groups.

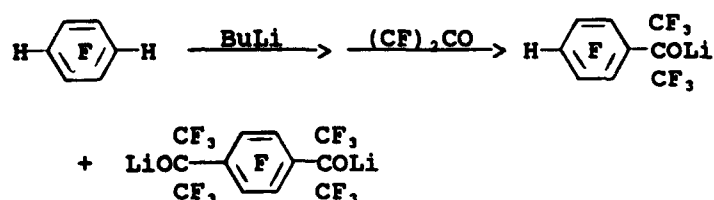


The X-ray crystal structure of this ring was obtained with a P2<sub>1</sub> Syntex diffractometer system using the Nicolet SHELXTL (Version 5.1) structure solution package. The crystal class is monoclinic with lattice constants of  $a = 11.836(4)\text{\AA}$ ,  $b = 13.856(5)\text{\AA}$ ,  $c = 14.658(7)\text{\AA}$ ,  $\beta = 102.38(3)^\circ$ , and  $V = 2,348(2)\text{\AA}^3$  based on 25 reflections in the range  $15 < 2\theta < 18$ . A total of 3,081 unique reflections were obtained with 1,472 with  $F > 3\sigma(F)$ . Refinement of 251 parameters yielded  $R = 0.1073$ ,  $R_w = 0.0683$  and  $\text{GOF} = 1.717$ .

## II. Year 2: May 1, 1992 - April 30, 1993

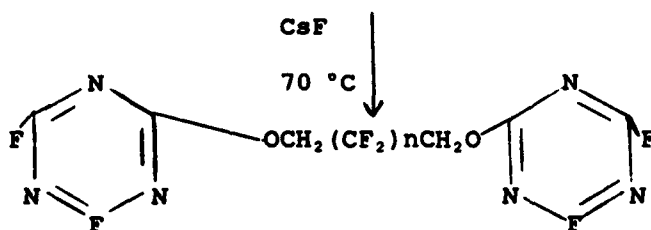
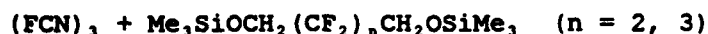
The importance of methods for the introduction of perfluorinated moieties into molecules is well known, but has historically been extremely difficult to achieve, primarily because of the dearth of transfer reagents with general applicability. We have developed, new, convenient and high yield synthetic methods for the preparation of previously difficult to obtain products, as well as routes to a variety of new and unusual compounds.

Some alcohols have been silylated to give the  $R_2OSi(CH_3)_3$  reagents or lithiated. These materials provide useful reagents for the preparation of per- and polyfluorinated aromatic ethers, e.g.,



We have extended the chemistry of these compounds to prepare aromatic oligomers containing the perfluoropropylidene group. Other useful reagents we have prepared include the alcohols  $\text{C}_6\text{F}_5\text{C}(\text{CF}_3)_2\text{OK}(\text{SiMe}_3)(\text{Li})$ , and the silylated derivatives of the alcohols  $\text{CH}_3(\text{CF}_3)_2\text{COH}$ , and  $(\text{CH}_3)_2\text{CF}_3\text{COH}$ .

The chemistry of polyfluorinated siloxanes has been used to derivatize cyanuric fluoride.

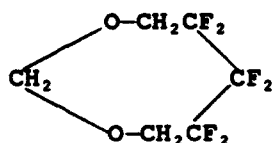
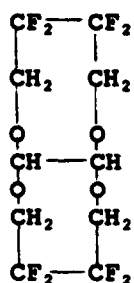
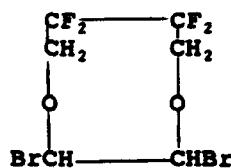
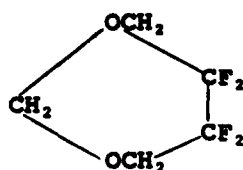


These products are obtained in high yield (75 - 87%) and in good purity, and are expected to exhibit properties useful in high temperature lubricant or hydraulic fluid applications.

A number of polyfluorinated cyclic ethers have been prepared from the reactions between  $(\text{CH}_3)_3\text{SiOCH}_2(\text{CF}_2)_n\text{CH}_2\text{OSi}(\text{CH}_3)_3$ , ( $n = 2, 3$ ) and  $\text{CH}_2\text{Br}_2$ , and

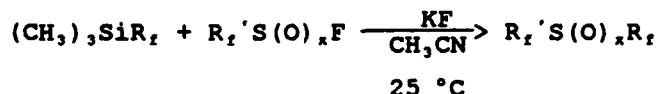


$\text{CHBr}_2\text{CHBr}_2$ , i.e.,



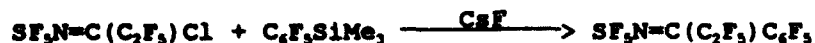
These new polyfluorinated heterocycles provide a unique opportunity to study the host/guest chemistry of medium sized polyfluorinated heterocycles. It may be possible to complex fluoride ion with these materials, which in turn would provide a useful additive(s) for the stabilization of high temperature fluids in metal systems at high pressure.

While much effort has been directed toward the perfluoroalkylation or perfluorophenylation of a variety of organic compounds, e.g., olefins (external & internal), aryls, esters, ketones, aldehydes, etc., in our study the methodology has been extended to perfluorinated internal azaalkenes and to simple sulfinyl or sulfuranyl compounds, e.g.,

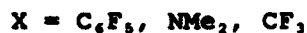
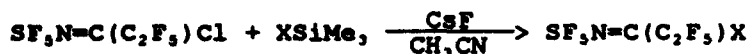


in the latter case to provide an excellent high yield route for the preparation of perfluoroalkyl or aryl sulfinyl fluorides, sulfonyl fluorides, sulfoxides and sulfuranes.

Azenes, for example  $\text{SF}_5\text{N}=\text{C}(\text{C}_2\text{F}_5)\text{Cl}$ , react with  $\text{C}_6\text{F}_5\text{SiMe}_3$  in the presence of anhydrous  $\text{CsF}$  to give the new pentafluorophenyl-substituted azenes in essentially quantitative yields.



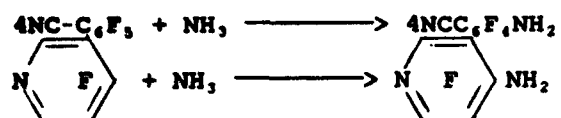
Also, other silylated reagents may be employed to give other azenes.



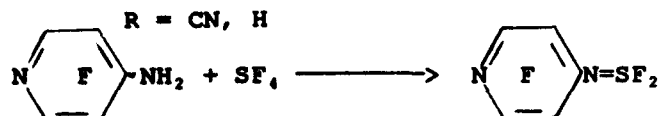
The chemistry of acyclic and heterocyclic perfluoro-N-vinylamines has been investigated extensively for the first time. The reaction of these compounds with electrophiles is equally facile when compared to those with nucleophiles even under very mild conditions. With nitrogen based nucleophiles such as ammonia, methyl- and 2,2,2-trifluoroethylamine,  $\text{R}_f\text{CHFCN}$  and  $\text{R}_f\text{CHF}(\text{CF}_3)=\text{NR}$  [ $\text{R}_f = \overline{\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{N}}$  or  $\overline{\text{CF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{N}}$  and  $\text{R} = \text{CH}_3$ , or  $\text{CH}_2\text{CF}_3$ ] are obtained, respectively. Formation of  $\beta$ -substituted perfluorovinylamines i.e.  $\text{R}_f\text{CF}=\text{CFR}$  [ $\text{R}_f = \overline{\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{N}}$  or  $\overline{\text{CF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{N}}$  and  $\text{R} = \text{CH}_3$ ,  $n\text{-C}_4\text{H}_9$ , or  $\text{N}(\text{CH}_3)_2$ ] is achieved using alkyl lithium or dimethylaminotrimethylsilyl reagents. Some of these derivatives have good potential as monomers for the little known perfluorovinylamine-copolymers. Reaction with electrophilic reagents such as  $\text{ClOSO}_2\text{F}$ ,  $\text{ClF}$  and  $\text{SF}_5\text{OCl}$  results in bidirectional addition to form isomers of the type  $\text{R}_f\text{CFXCF}_2\text{Cl}$  (I) and  $\text{R}_f\text{CFClCF}_2\text{X}$  (II) [ $\text{R}_f = \overline{\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{N}}$ ,  $\overline{\text{CF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{N}}$ ,  $\overline{\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{N}}$  or  $(\text{CF}_3)_2\text{N}$ ;  $\text{X} = \text{F}$ ,  $\text{OSO}_2\text{F}$  or  $\text{OSF}_3$ ]. However, in some cases only isomer (I) is obtained, e.g.,  $\overline{\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{NCF}(\text{OSO}_2\text{F})\text{CF}_2\text{Cl}}$ , from the reaction with  $\text{ClOSO}_2\text{F}$  as an addition product. When  $\text{CF}_3\text{OF}$  is added across these perfluorovinylamines, a single addition isomer  $\text{R}_f\text{CF}_2\text{CF}_2\text{OCF}_3$  is formed. With  $(\text{CF}_3)_3\text{COCl}$ , complete reversal of addition is observed on reaction with perfluorovinylpyrrolidine vis-a-vis perfluorovinylmorpholine. Although no reaction is observed thermally, photolytic reactions with  $\text{SF}_5\text{Cl}$  and  $(\text{CF}_3)_2\text{NCl}$  give  $\text{R}_f\text{NCFXCF}_2\text{Cl}$  [ $\text{R}_f = \overline{\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{N}}$  or  $\overline{\text{CF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{N}}$ ;  $\text{X} = \text{N}(\text{CF}_3)_2$  or  $\text{SF}_3$ ]. These derivatives are characterized by IR, NMR, and mass spectra, and elemental analyses. Our studies have also led to the development of synthetic routes to a variety of per- and polyfluorinated amines containing aromatic and/or alkyl groups and other heteroatoms including S and O.

Pentafluorobenzonitrile and other fluorinated substrates have been

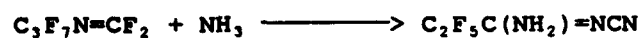
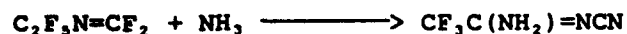
reacted with ammonia as shown below.



The chemistry of these primary amines is varied and interesting. Reaction with  $\text{SF}_4$  gives the corresponding, unstable sulfur difluoride imides.



More interestingly, when perfluoroazaalkenes are reacted under closely controlled conditions with  $\text{NH}_3$ , a class of compounds of which only a few examples are known, and whose chemistry has not been explored, is obtained.

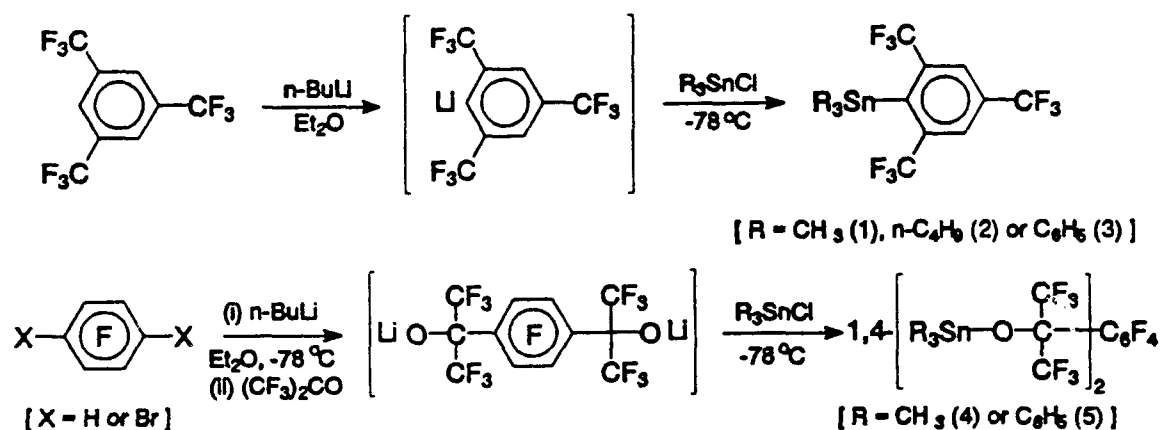


Both compounds are white, stable solids.

### III. Year 3: May 1, 1993 - April 30, 1994

The role of employing sterically and/or electronically demanding ligands to achieve kinetic stabilization of compounds with unusual oxidation/coordination numbers has attracted much attention from main group/transition metal chemists. These sterically demanding groups may be (a) substituted aromatic systems such as the tris(tert-butyl)phenyl (supermesityl), 2,4,6-tris(isopropyl)phenyl, pentamethylcyclopentadiene (Cp'), (b) highly substituted methyl systems, e.g., bis(trimethylsilyl)methyl and tris(trimethylsilyl)methyl, or (c) bulky imido ligands such as -Nmesityl(B(mesityl)<sub>2</sub>), -N(SiMe<sub>2</sub>Ph)<sub>2</sub> and -N(SiMe<sub>3</sub>)<sub>2</sub>.

The reactions of lithiated ligands, R<sub>2</sub>Li and R<sub>2</sub>'Li, provide easy access to the trifluoromethyl-containing organotin(IV) derivatives, 1 through 5.



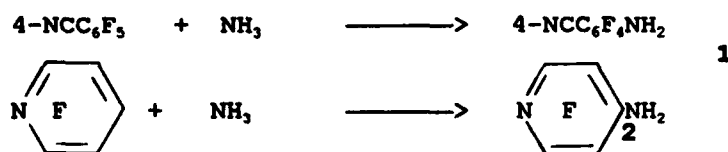
Crystals for compound 3 belong to a non-centrosymmetric (polar) space group Pna2<sub>1</sub>, which requires determination of absolute configuration. Due to the presence of the tin atom, which has an effective anomalous scattering effect, the absolute configuration of 3 is easily determined. Refinement of an additional parameter multiplying the imaginary components of the atomic scattering factors (delta-f values) indicates that the configuration initially assigned is incorrect. The enantiomorphous configuration is obtained by inversion of the original atomic coordinates. The final value of Roger's parameter<sup>19</sup> η = 0.93 with a small esd value of 12 supports the correctness of the absolute structure reported. This is supported by the lower R and R<sub>w</sub>

values of 0.0345 and 0.0401 for the absolute structure reported versus values of 0.0364 and 0.0435 for the alternate configuration.

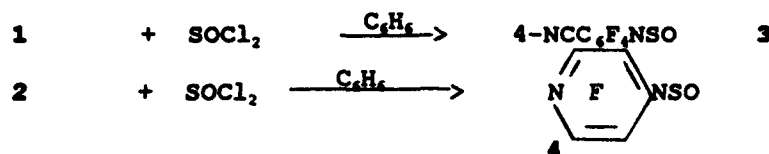
$\beta$ -Fluorosultones, precursors to fluorosulfonyl derivatives, find application in the production of strong sulfonic acids, ion-exchange resins, surface active agents and perfluorinated sulfonate ionomers. These compounds are prepared by the well documented reaction of  $\text{SO}_2$  with fluoroolefins, fluorovinyl ethers and, more recently, perfluorovinylsulfonylfluoride. In all these cases the carbon atoms in the four membered  $\beta$ -fluorosultone ring may be bonded to hydrogen, halogens, poly/perfluoroalkyl/alkoxy or fluoro sulfur(VI) substituents, in addition to fluorine. The conspicuous absence of a nitrogen substituent in  $\beta$ -fluorosultones, the reactive nature of perfluorovinylamines and the potential that fluoroamine containing sultones provide for the subsequent preparation of highly stable and unusual fluorinated conducting polymers, prompted us to explore the possibility of synthesizing the first nitrogen substituted  $\beta$ -fluorosultones.

There are four classes of fluorine-containing compounds with double and triple bonds between sulfur (IV) and nitrogen, i.e.,  $\text{N}=\text{SX}$ ,  $\text{RN}=\text{S}=\text{O}$ ,  $\text{RN}=\text{S}=\text{NR}$  and  $\text{RN}=\text{SX}_2$ . Of the first type, only  $\text{N}=\text{SF}$  and  $\text{N}=\text{SCl}$  are known. A wide variety of N-sulfinyl compounds,  $\text{RN}=\text{S}=\text{O}$ , sulfur diimides,  $\text{RN}=\text{S}=\text{NR}$ , as well as numerous compounds of the type  $\text{RN}=\text{SX}_2$  ( $\text{X} = \text{Cl}$ ,  $\text{F}$  or organic substituent) are in the literature.

A large number of sulfur difluoride imides ( $\text{RN}=\text{SF}_2$ ) are useful as precursors to other nitrogen-sulfur compounds. Their syntheses continue to be of interest. The two aromatic amines 1, 2 are synthesized.

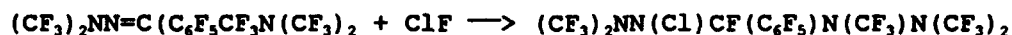


These primary amines react with thionyl chloride to give the respective N-sulfinyl compounds in essentially quantitative yield.



Silylated perfluoroalkyl and perfluoroaryl compounds  $\text{R}_3\text{SiR}_f$  ( $\text{R}$  = alkyl;  $\text{R}_f$  = F-alkyl or F-aryl) are remarkably stable and easily prepared. These compounds are powerful transfer reagents when reacted with active electrophiles in the presence of an alkali metal fluoride resulting in the concomitant substitution of the trialkylsilyl group. While these species have been known for many years, it is only recently that their roles as valuable precursors to highly fluorinated inorganic and organic compounds have been exploited. The methods for introduction of perfluorinated alkyl and aryl groups into other compounds are fraught with difficulty either because the precursors are unstable, or require special synthetic conditions, or are potential health hazards. However, now given the ready accessibility of silylated perfluoroalkyl and aryl compounds, many difficult syntheses are readily accomplished in the presence of fluoride ion.

The azene  $(\text{CF}_3)_2\text{NN}=\text{C}(\text{Cl})\text{N}(\text{CF}_3)_2$  is reacted with  $\text{C}_6\text{F}_5\text{SiMe}_3$  to give  $(\text{CF}_3)_2\text{NN}=\text{C}(\text{C}_6\text{F}_5)\text{N}(\text{CF}_3)_2$ . In our continuing effort to synthesize solid tetrazanes that would be suitable for X-ray crystal structure determination, this aromatic azene was reacted with  $\text{ClF}$  and the product photolyzed.



Unfortunately upon photolysis only decomposition occurs and no tetrazane was found.

Cycloaddition, via nucleophilic attack on fluorinated precursors, plays an important role in the synthesis of fluoroheterocycles. In an earlier study of reactions of 1,2-dichloroperfluorocycloalk-1-enes (alkene = butene, pentene, hexene) with  $\text{N,N}'$ -dimethyl-ethylenediamine, we reported that singly N-substituted products  $\text{H}_3\text{CNH}(\text{CH}_2)_2\text{N}(\text{CH}_3)\overline{\text{C}=\text{C}(\text{Cl})(\text{CF}_2)_n\text{CF}_2}$  ( $n = 2, 3$ ) undergo intramolecular cyclization to produce spiro derivatives,  $\text{H}_3\text{CN}(\text{CH}_2)_2\text{N}(\text{CH}_3)\overline{\text{CC}(\text{Cl})=\text{CF}(\text{CF}_2)_n}$ , ( $n = 1, 2$ ), with concomitant elimination of

fluoride ion. Polymerization rather than cyclization occurs in the case of the cyclobutene derivative of the diamine,  $\text{H}_2\text{CNH}(\text{CH}_2)_2\text{N}(\text{CH}_3)\overline{\text{C}=\text{C}(\text{Cl})\text{CF}_2\text{CF}_2}$ .

Intramolecular cyclization with concomitant  $\beta$ -elimination of an allyl fluoride ion in the presence of a suitable base may prove to be a convenient way of synthesizing fluoroheterocycles. In view of this, we react 1,2-dichloroperfluorocycloalk-1-enes-1 (alkene = butene, pentene) with the difunctional nucleophiles, 2-mercaptoethanol,  $\text{HO}(\text{CH}_2)_2\text{SH}$ , and 1,2-ethanedithiol,  $\text{HS}(\text{CH}_2)_2\text{SH}$ , respectively (See Figure I for compound identification). In reactions of  $\text{HO}(\text{CH}_2)_2\text{SH}$  with the chlorofluoroalkenes, depending on the stoichiometric ratio, either singly ((1) and (4)) or doubly ((2) and (5)) substituted products are obtained. This is not unexpected, since it is well known that displacement of both chloride ions is possible when a strong nucleophilic reagent, such as a mercaptide anion, is employed. In the presence of triethylamine, both 5-membered ring compounds (1) and (2) convert readily into their spirocyclic components, (7) and (8), respectively. This intramolecular cyclization proceeds more slowly with the 4-membered ring derivatives. Complete conversion of compound (4) into (10), or (5) into (11), does not occur after two weeks at 25 °C. However, in contrast to the cyclobutene derivative of the diamine, polymerization does not occur.

In our work, when ethanedithiol is reacted with the 5-membered cyclic olefin,  $\text{Cl}\overline{\text{C}=\text{C}(\text{Cl})(\text{CF}_2)_2\text{CF}_2}$ , the likely intermediate, the 1-( $\text{SCH}_2\text{CH}_2\text{SH}$ ) derivative is not observed and regardless of the reactant ratio only a singly substituted spiro derivative (3) is isolated. However, with the 4-membered cyclic alkene  $\text{Cl}\overline{\text{C}=\text{C}(\text{Cl})\text{CF}_2\text{CF}_2}$ , an inseparable mixture of either 6(a) and 6(b) or 6(b) and 6(c), depending on the reaction ratio of 1:1 or 2:1 of dithiol to cyclic alkene, is obtained. Others have demonstrated that owing to the ability of sulfur, but not oxygen, to stabilize adjacent centers of negative charge, the two nucleophiles react via two different pathways which lead to formation of dissimilar products. Similarly our study indicates that due to the greater polarizability of the electron pairs on sulfur, nucleophilic displacement of the vinyl chlorine at C-1 followed by attack of the thiolate

anion again at C-1 occurs to form the spiro derivatives (3) and (6a).

Isolation of compound 6(b) but not the analogous cyclopentene derivative is in keeping with our experience with the rates and products found for the reaction of  $RN(H)CH_2CH_2N(H)R$  with dichlorotetrafluorocyclobutene and dichlorohexafluorocyclopentene.

It is interesting to note that double intramolecular cyclization does not occur to produce the dispiro derivative (9) when (2) is treated with excess triethylamine for an extended period of time at 25 °C. Heating (2) in THF for several days with  $K_2CO_3$ , only produces its monospiro derivative (8). However, brief refluxing of (2) with  $K_2CO_3$  in a more polar solvent with a higher b.p., such as DMF, although resulting mainly in decomposition, does produce a small amount of the dispiro derivative (9). The carbon-carbon double bond infrared stretching mode of (9) has shifted to a much higher frequency,  $1756\text{ cm}^{-1}$ , compared to the monospiro compound (8) at  $1656\text{ cm}^{-1}$  which in turn, is higher than  $1543\text{ cm}^{-1}$ , the stretching frequency of the parent molecule (2).

We have also found that dichloroperfluorocycloalkenes react with a variety of macrocyclicamines to give perfluorocycloalkenyl substituted macrocycles. The products are characterized by NMR, IR, MS, and elemental analysis. Single crystal X-ray analyses of 1,4,7-tris(chlorotetrafluorocyclobutenyl)-1,4,7,10-tetraazacyclododecane and 1,7-bis(chlorohexafluoropentenyl)-1,4,7,10-tetraazacyclododecane have been obtained.

The first detailed investigations on the reactions of polyfluoromono- and dialkoxysilanes with cyclic fluorophosphazenes was carried out and compared with reactions of the nonfluorinated analogues. The method offers an easy and elegant route to the hitherto poorly studied bridged and dangling phosphazene compounds. Single crystal X-ray structure analyses of  $(CF_3CH_2O)_2N_3P_3F_6$  and  $(4-FC_6H_4O)_3P_3N_3OCH_2CF_2CF_2CH_2ON_3P_3(4-FC_6H_4O)_3$  were obtained.

Reactions of  $N_3P_3F_6$  with  $[CF_2CH_2OSiMe_3]_2$  and  $CF_2[CF_2CH_2OSiMe_3]_2$  in the presence of CsF as catalyst are found to proceed readily under mild conditions to yield the monospiro and the bridged fluorophosphazene derivatives

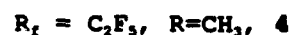
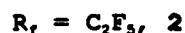


$(\text{CF}_3\text{CH}_2\text{O})_2\text{N}_2\text{P}_2\text{F}_4$ ,  $\text{CF}_2(\text{CF}_2\text{CH}_2\text{O})_2\text{N}_2\text{P}_2\text{F}_4$ ,  $\text{F}_3\text{N}_2\text{P}_2\text{OCH}_2(\text{CF}_2)_2\text{CH}_2\text{ON}_2\text{P}_2\text{F}_5$ , and  $\text{F}_3\text{N}_2\text{P}_2\text{OCH}_2(\text{CF}_2)_2\text{CH}_2\text{ON}_2\text{P}_2\text{F}_5$  in good yields. Subsequent reactions of the bridged derivative with 4- $\text{FC}_6\text{H}_4\text{OSiMe}_3$ , 3- $\text{FC}_6\text{H}_4\text{OSiMe}_3$ , and  $\text{CF}_3\text{CH}_2\text{OSiMe}_3$  give the additional substitution products  $(4\text{-FC}_6\text{H}_4\text{O})_2\text{P}_2\text{N}_2\text{OCH}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{ON}_2\text{P}_2(4\text{-FC}_6\text{H}_4\text{O})_2$ ,  $(3\text{-FC}_6\text{H}_4\text{O})_2\text{P}_2\text{N}_2\text{OCH}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{ON}_2\text{P}_2(3\text{-FC}_6\text{H}_4\text{O})_2$ , and  $(\text{CF}_3\text{CH}_2\text{O})_2\text{P}_2\text{N}_2\text{OCH}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{O}$ , and an incompletely characterized dispiro bridged moiety with the facile elimination of  $\text{Me}_3\text{SiF}$ . The reaction of  $\text{Me}_3\text{SiO}(\text{CH}_2)_3\text{OSiMe}_3$  with  $\text{N}_2\text{P}_2\text{F}_4$  in the presence of  $\text{CsF}$  gives the monospiro, dangling and the bridged derivatives in varying yields depending upon the reaction parameters. Reactions of  $\text{N}_2\text{P}_2\text{F}_4$  with excess  $\text{CF}_3\text{CH}_2\text{OSiMe}_3$  in the presence of catalytic amounts of  $\text{CsF}$  or  $\text{N}_2\text{P}_2\text{Cl}_4$  with excess  $\text{KF}$  and  $\text{CF}_3\text{CH}_2\text{OSiMe}_3$  in the absence of solvent proceed at  $80^\circ\text{C}$  to yield  $[\text{CF}_3\text{CH}_2\text{O}]_2\text{N}_2\text{P}_2$  and  $\text{Me}_3\text{SiF}$ .

Our interest in cyclic fluorophosphazene chemistry stems in part from our recent success in the reactions of perfluoroaromatic compounds with cyclic and acyclic polyfluoroalkoxy and aryloxy siloxanes. These reactions show the formation of stable C-O bonds in the presence of fluoride ion as catalyst with concomitant facile elimination of silyl fluorides. The bridged derivatives are described as model compounds for condensation polymerization studies involving phosphazenes. The transformation of bridged cyclic phosphazenes to spiro phosphazenes is documented for the first time and is followed by  $^{19}\text{F}$  NMR studies. A dangling species is isolated and its role as an intermediate in the formation of the bridging and spiro compounds is suggested.

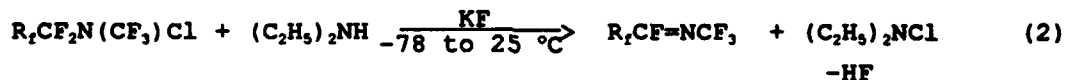
Dichloro(perfluoroalkyl)amines,  $\text{R}_2\text{NCl}_2$ , are reactive compounds whose synthesis is relatively straightforward. Metathetical replacement of the two chlorine atoms by other elements or groups provides a simple route to interesting compounds. The lability of fluorine bonded to the  $\alpha$ -carbon in per or polyfluoroalkyl-containing nitrogen compounds is markedly enhanced. In fact, in some cases fluorine atoms in the  $\alpha$  position are effective as fluorinating species. Therefore, it is of interest to investigate the behavior of  $\text{R}_2\text{CF}_2\text{NCl}_2$  toward protic nucleophiles.

The reactions of N,N-dichloro(pentafluoroethyl)amine (1) and N,N-dichloro-(heptafluoropropyl)amine (2) with secondary amines in a 1:2 molar ratio in the presence of KF result in the formation of N-chloro-1-dialkylamino(perfluoroalkyl)imines in 60% yield. The N-chloro(dialkyl)amines are also isolated and identified based on their spectral data (see experimental section). The same results are obtained in the absence of KF provided that more dialkylamine is added to absorb the HF formed during the reaction.



It is observed that the yields of 3, 4 and 5 depend on the molar ratio of the reactants. Higher yields are obtained when more dialkylamine is used.

Another example of such dependence is found when monochloroamines  $C_2F_5N(CF_3)Cl$  (6) and  $C_3F_7N(CF_3)Cl$  (7), in which one chlorine atom of 1 and 2 is replaced by a trifluoromethyl group, are reacted with  $(C_2H_5)_2NH$ . If equimolar amounts of monochloroamine and dialkylamine are used, only the respective perfluoroazaalkenes and N-chloro(dialkyl)amines are formed, viz.,

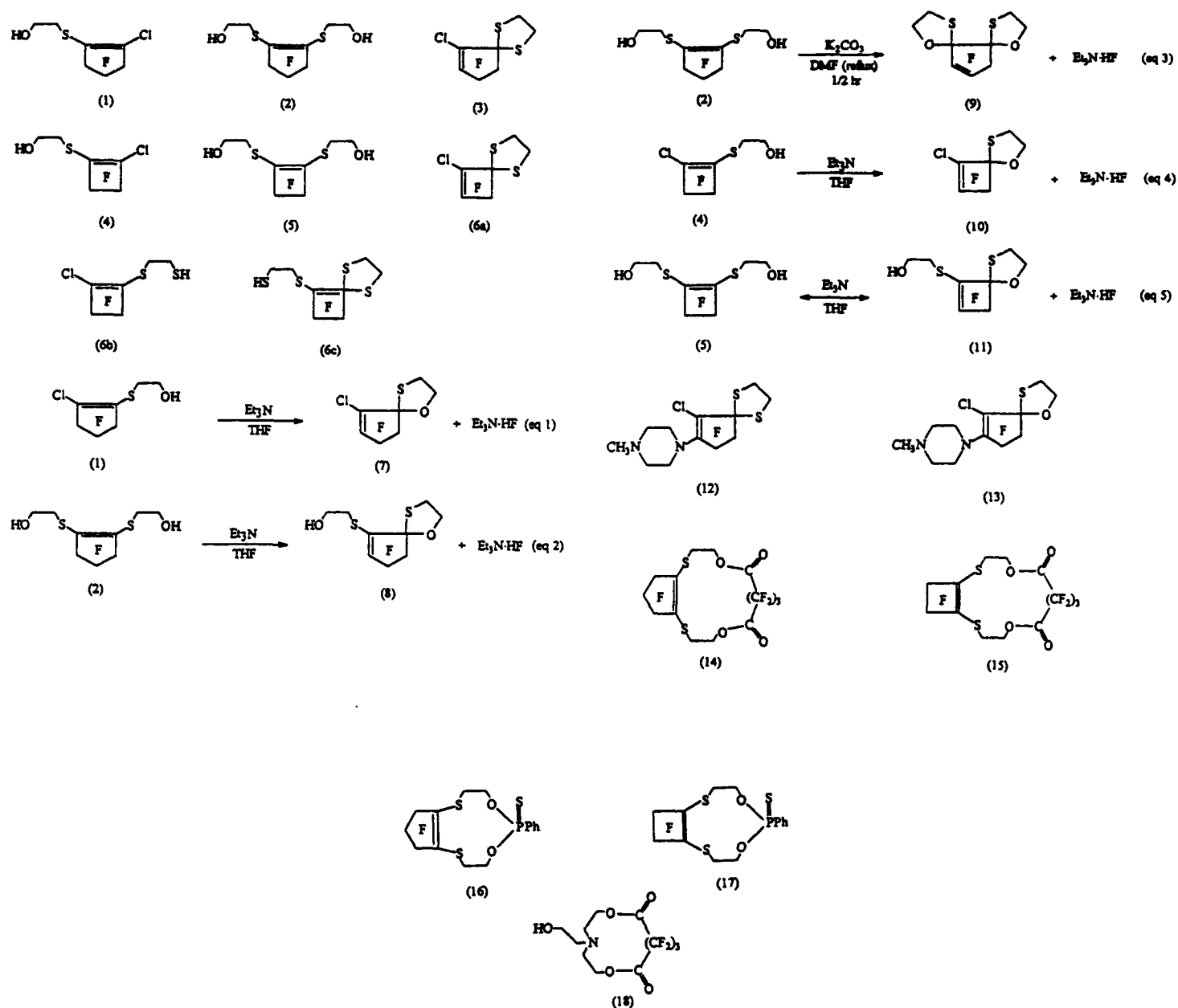


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Compounds 8 and 9 are formed essentially quantitatively. If excess of the dialkylamine is used, the corresponding N-dimethylamido(perfluoroalkyl)imine (11) is obtained.

Figure 1. Compound Identification



#### IV. Publications Resulting All or in Part from Support of AFOSOR 91-0189

##### Papers Published:

- M. K. Alam, B. Scott, R. L. Kirchmeier and J. M. Shreeve, "Preparation of New Phosphoranes  $(C_6H_5)_2P(O)NHC_6F_5$  and  $C_6H_5P(O)(NHC_6F_5)_2$ , 1,3-Bis(pentafluorophenyl)-2,4-diphenyl-1,3,2,4-diazadiphosphetidine  $(C_6H_5PNC_6F_5)_2$ , and 1,3-Bis(2-fluorophenyl)-2,4-diphenyl-2,4-dioxo-1,3,2,4-diazadiphosphetidine  $(C_6H_5P(O)NC_6H_4F)_2$ ," European Journal of Solid State and Inorganic Chemistry, 28, 847 (1991).
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#### Papers Accepted for Publication

- R. D. Verma, R. L. Kirchmeier and J. M. Shreeve, "Chemistry of Pentafluorosulfanyl Compounds," accepted for publication in *Advances in Inorganic Chemistry* (1993).
- Q. C. Mir and J. M. Shreeve, "Reactions of 1,2-Dichlorohexafluoro-cyclopent-1-ene with 2-Mercaptoethanol and Ethanedithiol and of Their Products," *Journal of Fluorine Chemistry*, (1994).
- Y. F. Zhang, R. L. Kirchmeier and J. M. Shreeve, "Reaction of Hexafluorobenzene with Trimethylsilyl Ethers," *Journal of Fluorine Chemistry*, (1994).

### Papers Prepared

- A. J. Elias, R. L. Kirchmeier and J. M. Shreeve, "Polyfluoroalkoxy and Aryloxy Cyclic Phosphazenes: An Alternative Synthetic Route to Substitution Reactions Using Siloxanes in the Presence of Fluoride Ion Catalysts," Inorganic Chemistry, submitted for publication (1994).
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- J. Chen, A. Sandu, R. L. Kirchmeier and J. M. Shreeve, "Studies on the Reactions of Dichloro(perfluoroalkyl)amines With Protic Nucleophiles," Inorganic Chemistry, submitted for publication (1994).
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V. Graduate Students/Post-Doctoral Students Who Have Worked on this Research

#### Post-Doctoral Students

O. D. Gupta  
E. O. John  
N. R. Patel  
Y.-F. Zhang  
A. Sandhu  
C.-Y. Guo  
Y.-Y. Zheng  
A. Elias  
A. Vij  
B. Krumm  
S. Ritter  
M. Nishida

#### Graduate Students

Yihong Chen  
Jian-guo Chen

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